Sodium/Calcium Exchange in Montmorillonite and Illite Suspensions[1]

I. Shainberg, J. D. Oster, and J. D. Wood[2]

ABSTRACT

The effect of salt concentration and exchanger composition on Na/Ca exchange in montmorillonite and illite suspensions (0.02 to 0.08 g clay/g water) was studied, where the equivalent fraction of exchangeable Ca, E_{Ca}, ranged from 0.6 to 1. A theoretical evaluation based on double-layer theory for montmorillonite indicates that the formation of tactoids and internal surfaces at the Ca^{2+} end of the exchange isotherm can cause the Vanselow selectivity coefficient, K_v, to depend on exchangeable cation composition and total electrolyte concentration. Whereas for montmorillonite, K_v increased with E_{Ca} (0.6 < E_{Ca} < 1), as predicted for internal surfaces, the reverse was true for illite, where external surfaces predominate. Likewise, for a given Na adsorption ratio, dilution of the equilibrium solution for illite (0.6 < E_{Ca} < 1) and for montmorillonite (E_{Ca} ≃ 0.6) decreased K_v as predicted for external surfaces.

The average Gapon selectivity coefficient for the montmorillonite (0.011) and illite clays (0.023) with E_{Ca} ≤ 0.8, suggests that the value for soils, (0.0148) reflects their mixed mineralogy.

Additional Index Words: quasicrystals (tactoids), external and internal surfaces, Gapon selectivity coefficient, Vanselow selectivity coefficient, adsorption ratio.

C ATION-EXCHANGE EQUATIONS describe the distribution of cations between the exchanger phase and its equilibrium solution. Several approaches have been used in deriving these equations. The formal thermodynamic treatment, based on the mass action principle, gives no direct information about the molecular mechanisms and forces operating in the system. Another approach, based on the diffuse double-layer theory, consists of a molecular description of the coulombic forces which are operative in the process of exchange. Discrepancies between the experimental results and those predicted by the diffuse double-layer theory facilitate the evaluation of the magnitude of other forces acting in the Na/Ca ionic distribution on clay surfaces. In this study, the effect of the presence of the Ca quasicrystals on the ionic distribution is considered. Also, the equations based on the thermodynamic and the diffuse double-layer approach are compared with the empirical Gapon equation (U. S. Salinity Laboratory Staff, 1954).

Here we report the effect of solution phase composition on that of the exchanger phase for Ca/Na equilibrium on Wyoming montmorillonite and Fithian illite in the range of exchangeable Na fraction, E_{Na}, commonly found in agricultural soils (E_{Na} ≤ 0.40). Since in this range montmorillonite forms quasicrystals or tactoids (Shainberg and Otoh, 1968), we expected that the presence of internal surfaces would affect the selectivity coefficient. The differences in the cation

exchange selectivity coefficients between the two clays were analyzed according to the various theories and the application of the findings to the ionic equilibria of saline soils was evaluated.

Theoretical Considerations

For the exchange reaction

$$2\ NaX + Ca^{2+} = CaX_2 + 2\ Na^+ \qquad [1]$$
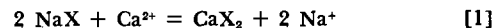
the thermodynamic exchange equilibrium constant coefficient is represented by

$$K = \frac{(Na^+)^2\ (CaX_2)}{(NaX)^2\ (Ca^{2+})} \qquad [2]$$

where X is one equivalent of the anionic part of the exchanger and () refers to the activity of the chemical species. The value of K in Eq. [2] is independent of the convention used in formulating the exchange reaction. Sposito (1977) showed that whether the adsorbed cations are designated to react in molar quantities (the Vanselow convention) or in equivalents (the Gapon convention), both arbitrary conventions lead to the same value of the thermodynamic equilibrium constant.

In Eq. [2], only the activity of the cations in the solution phase is easily computed in terms of molar ion concentration, m, and molar activity coefficient, γ. The activity of a species in the adsorbed phase is not as easily computed. If it is assumed that the exchangeable cations' activities are equal to their equivalent fractions, then the Gaines-Thomas selectivity coefficient, K_{GT}, is obtained

$$K_{GT} = \frac{E_{Ca}\ m_{Na}^2\ \gamma^2_{Na}}{(E_{Na})^2\ m_{Ca}\ \gamma_{Ca}} \qquad [3]$$

where E_{Na} and E_{Ca} are the equivalent fractions of the total exchange capacity occupied by the ions specified.

If the activity of an exchangeable cation is equal to its mole fraction, N, Eq. [2] gives the Vanselow selectivity coefficient, K_v

$$K_v = \frac{N_{Ca}\ m_{Na}^2\ \gamma^2_{Na}}{(N_{Na})^2\ m_{Ca}\ \gamma_{Ca}}. \qquad [4]$$

In a recent paper Sposito and Mattigod (1979) showed that for the exchange reaction of Na with trace metal cations ($M = Cd^{2+}$, Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}) on Camp Berteau montmorillonite, K_v was constant and independent of the exchanger composition for E_M < 0.7. This observation indicated to them that the Vanselow selectivity coefficient was valid; that the cationic mixture on the exchanger phase behaved as an ideal mixture, i.e., the activity of each adsorbed ion was equal to its mole fraction; and that the activity coefficient of each adsorbed ion was equal to one.

van Bladel et al. (1972), studying Na/Ca exchange on Camp Berteau montmorillonite, found an almost constant K_{GT} at E_{Ca} < 0.7. However, as they pointed out, "the most striking feature about Na/Ca exchange is the more pronounced selectivity of the clay for Ca^{2+} ions at the calcium-rich end isotherms." Levy and Hillel (1968) reached the same conclusions for montmorillonite soils. van Bladel et al. (1972) also reported an increased affinity for Ca^{2+} in terms of the selectivity coefficient as salt concentration decreased at the Ca-rich end isotherm. This range of Ca saturation is typical of agricultural soils and therefore is of high interest.

Does the diffuse double-layer theory provide an explanation for these observations? Babcock (1963) showed that the theory for external planar surfaces predicts an increased affinity by the clay for Ca^{2+} as the electrolyte concentration increases and decreased affinity for Ca^{2+} as E_{Ca} increases. The experimental data do not follow both predictions, as he already noted (Babcock, 1963). However, Shainberg and Otoh (1968) and Bar-On et al. (1970) observed that at E_{Ca} > 0.6, montmorillonite platelets condense into packets of platelets, consisting of 4 to 8 platelets in a packet with a film of water 0.45-nm thick on each internal surface. The presence of internal surfaces within

the packets may explain the experimental changes in the selectivity coefficients with changes in E_{Ca} and electrolyte concentration in the system.

Eriksson (1952) developed an exchange equation for mono- and divalent ions from the diffuse double-layer theory. Eriksson's equation may be written:

$$\frac{\Gamma_{Na}}{\Gamma} = \frac{r}{\Gamma(B)^{\frac{1}{2}}} \sinh^{-1} \frac{\Gamma \sqrt{B}}{r + 4\ V_d\ (m_{Ca})^{\frac{1}{2}}} \qquad [5]$$

in which

$$r = \frac{m_{Na}}{(m_{Ca})^{\frac{1}{2}}} \qquad [6]$$

is called the "reduced ratio", Γ is the surface charge density in meq/cm^2, Γ_{Na} is the portion of the surface charge density satisfied by the sodium ions, m represents the molar concentration of the subscript ion, and

$$B = \frac{8,000\ \pi\ F^2}{DRT} \qquad [7]$$

where $F = 2.89 \times 10^{11}$ esu/meq, D is the dielectric constant, R the molar gas content, and T is the absolute temperature. For water systems at 25°C, $B = 1.080 \times 10^{15}$. V_d is defined by

$$V_d = \cosh Y_d \qquad [8]$$

where Y_d is the dimensionless potential function in the plane midway between the platelets. In most applications of Eq. [5] (Bolt, 1955; Bower, 1959), it was assumed that the platelets are an infinite distance from each other where $Y_d = 0$, and Y_d is equal to 1.0.

The dimensionless potential function in the plane midway between the platelets within a tactoid is a function of the salt concentration and can be calculated from the diffuse double-layer theory (van Olphen, 1977). We realize that the accuracy of the diffuse double-layer calculations for the small distance between the platelets (0.9 nm) within a tactoid is limited. The theory involves the assumptions of uniformly charged surfaces, ions as point charges, ideal ionic solutions, etc. (van Olphen, 1977). These assumptions are not valid at small distance from the clay surface. However, the trend superimposed on the cation exchange equations as a result of tactoid formation should be evident. In the following calculations it is assumed that the internal surfaces are Ca-saturated, the surface charge density is 1.3×10^{-7} meq cm^{-2} (van Olphen, 1977), and the activity coefficients of the ions in the solution and exchange phase are 1. The calculated value for Y_d are presented in Table 1 together with the values for the Vanselow selectivity coefficient on both the external and internal surfaces.

On external surfaces the affinity of the clay for Ca^{2+} decreases (lower K_V) with increasing calcium saturation or decreasing E_{Na}. The Vanselow selectivity coefficient decreases from 0.80 at $E_{Na} = 0.58$ to 0.41 at $E_{Na} = 0.24$ for the $0.001M$ solutions and a similar trend exists for the higher concentrations. This effect is readily explained in terms of the electrostatic forces. The preference of the cation exchanger for Ca^{2+} increases with an increase in the negative electric potential in the diffuse double layer. The negative electric potential in the diffuse double-layer is reduced with an increase in the fraction of adsorbed Ca ions. Thus, the affinity of the clay for the divalent cation (competing with the monovalent ions) also diminishes. Also, the affinity of the clay for Ca^{2+} increases with increasing electrolyte concentration. Compressing the ions in the diffuse double layer leads to stronger interaction between the divalent cation and the negative surface, and more Ca^{2+} is adsorbed.

The affinity of the internal surfaces for Ca^{2+} is between 2 to 15 times (depending on the exchanger composition and the electrolyte concentration—see Table 1), that of the external surfaces. This effect is readily explained by the electrostatic forces. With the overlapping of the diffuse double layers, the negative electric potential also increases and the divalent ion is strongly attracted into the internal space. For internal surfaces, the affinity of the clay for Ca^{2+} decreases with an increase in salt concentration. With an increasing salt concentration, Y_d decreases, and the divalent Ca ion is more affected by the changes in the electrical potential than the monovalent Na ion. Also, the affinity of the clay for Ca^{2+} increases with increasing Ca saturation in agreement with the experimental results reported by van Bladel et al. (1972) and Levy and Hillel (1968). However, it should be pointed out that the diffuse double-layer

Table 1—Na/Ca selectivity coefficient (K_V) as predicted by the diffuse double-layer theory for external and internal surfaces.

R_{Na}	Total chloride concentration	External surfaces[†]		Internal surfaces		
		E_{Na}	K_V[‡]	Y_d	E_{Na}	K_V[‡]
	mol liter^{-1}					
10	0.001	0.24	0.41	6.5	0.062	6.50
	0.010	0.22	0.48	4.2	0.069	5.28
	0.100	0.16	0.90	2.0	0.092	2.95
20	0.001	0.39	0.55	6.5	0.180	2.96
	0.010	0.37	0.60	4.2	0.186	2.84
	0.100	0.31	0.92	2.0	0.201	2.29
30	0.001	0.58	0.80	6.5	0.405	2.04
	0.010	0.57	0.83	4.2	0.409	2.03
	0.100	0.52	1.08	2.0	0.408	2.03

[†] $Y_d = 0$.
[‡] Ion activity coefficients in the solution and exchanger phases were assumed to equal 1.

calculation (Table 1) may be misleading. In these calculations it was assumed that Y_d, for a given salt concentration, was constant and independent of E_{Ca}. It is probable that this potential also diminishes with increasing E_{Ca} and the affinity of the internal surfaces for Ca^{2+} does not increase with E_{Ca} as much as the calculation shows.

It is evident that the effects of salt concentration and degree of Ca saturation on K_V depend on the type of the surface (external vs. internal). In illitic and kaolinitic soils, where external surfaces predominate, an increase in Ca saturation, at a given concentration, will decrease K_V. Conversely, in montmorillonitic soils for an E_{Ca} range where tactoids are formed ($E_{Ca} > 0.7$), an increase in E_{Ca} should increase K_V. Similarly, the effect of concentration, at constant Na adsorption ratio, R'_{Na},[3] should vary, depending on the clay. In soils of mixed mineralogy, it is possible that the net effect will be that both the solution composition and the solution concentration have no effect on the selectivity coefficient.

MATERIALS AND METHODS

Clay-size fractions of Wyoming montmorillonite (API 25) and Fithian illite (API 35) were separated from larger size fractions by sedimentation. Na- and Ca-montmorillonite were prepared by equilibration with $1M$ solutions of NaCl and CaCl$_2$. Then, the clay was washed with distilled water by centrifugation until an AgNO$_3$ test indicated that the equilibrium solution was free of chloride. The salt-free gel was freeze-dried and stored in a desiccator. Na illite was prepared by repeated equilibration (two times) of the clay with $1M$ NaAOC solutions adjusted to a pH of 6.0 with HOAc. Thereafter, the Na illite was equilibrated with $1M$ solutions of NaCl or CaCl$_2$, washed with distilled water, and freeze-dried in the manner described for the montmorillonite clays. This procedure was followed to remove the CaCO$_3$ that contaminated the reference clay. Na/Ca clay suspensions with exchangeable Na fractions (E_{Na}) of 0.10, 0.20, and 0.40 were prepared by adding the appropriate amounts of homoionic dry clays to Na/Ca salt solutions of equal R'_{Na}. Two concentrations of clay suspensions were studied: 2.0 and 4.0% clay (wt/vol) for montmorillonite clay and 4.0 and 8.0% clay for illite suspensions. The salt solution concentrations were 3, 10, 30, 60, and 100 meq/liter. The clay gels were shaken for 1 hour and thereafter centrifuged. The ionic composition of the supernatant was analyzed according to standard methods. The exchangeable ions were extracted from the clay fraction using solutions of $1.0N$ MgOAc at pH 6. The ionic concentrations of the extract were analyzed and soluble Na and Ca ions were calculated from the chloride concentration and the known composition of the equilibrium solutions.
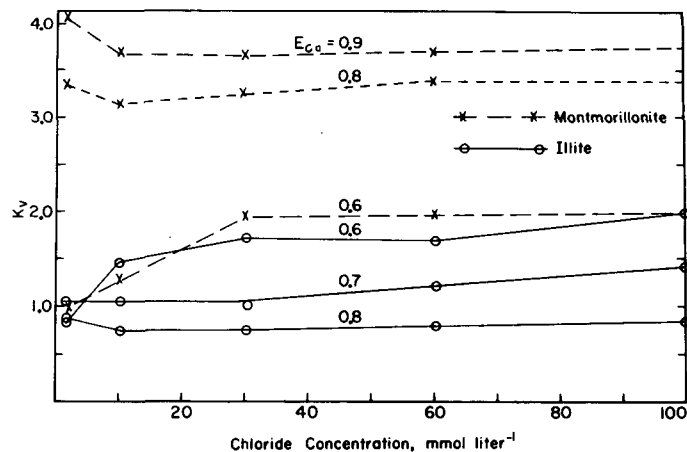
RESULTS AND DISCUSSION

The composition of the equilibrium solution and of the exchangeable ions are presented in Table 2. Two Na adsorption ratios are given, based on total

[3] $R'_{Na} = m'_{Na}/m'_{Ca}$, where the ion concentrations are expressed in mmol liter^{-1}.

Table 2—The composition of the equilibrium solutions and the exchanger phase.

Initial R'Na and ENa×100	Chloride concentration	R'Na	RNa	NaX	CaX	CEC	CEC (avg)	ENa
	mol liter⁻¹	(mmol liter⁻¹)¹/²			meq/100 g			
				Illite				
10	0.003	5.9	6.2	1.89	16.2	18.0	17.7	0.105
	0.010	8.2	9.1	3.03	15.4	18.4		0.165
	0.030	8.7	10.1	3.28	14.7	17.9		0.183
	0.060	9.1	10.9	3.28	14.2	17.5		0.187
	0.100	9.2	11.3	3.10	13.4	16.5		0.188
20	0.003	11.5	12.2	3.19	13.8	16.9	17.6	0.188
	0.010	15.3	16.8	4.39	13.4	17.8		0.247
	0.030	16.3	18.8	5.23	12.9	18.2		0.247
	0.060	17.6	21.0	5.17	12.9	18.0		0.286
	0.100	18.6	22.7	5.00	12.4	17.3		0.289
40	0.003	18.8	19.9	5.42	10.9	16.3	16.9	0.332
	0.010	27.1	29.6	6.26	11.1	17.4		0.361
	0.030	31.4	36.1	7.16	10.8	18.0		0.399
	0.060	32.6	38.6	7.00	9.3	16.3		0.429
	0.100	36.3	44.2	7.24	9.1	16.3		0.443
				Montmorillonite				
10	0.003	5.8	6.1	5.0	99.2	104.2	105.8	0.048
	0.010	8.8	9.5	8.4	99.0	107.4		0.078
	0.030	9.2	10.5	8.8	98.0	105.8		0.089
	0.060	9.1	10.8	9.3	96.2	105.5		0.088
	0.100	9.5	11.7	9.7	95.5	105.2		0.092
20	0.003	12.8	13.6	11.7	88.4	100.1	101.4	0.117
	0.010	14.6	16.0	14.5	88.3	102.8		0.141
	0.030	16.5	18.9	16.4	84.4	100.8		0.163
	0.060	17.0	20.2	17.4	84.0	101.4		0.171
	0.100	18.3	22.4	19.2	82.9	102.2		0.188
40	0.003	20.5	21.7	30.1	60.4	90.5	96.2	0.333
	0.010	23.0	25.5	30.1	60.3	90.4		0.333
	0.030	29.0	33.5	35.1	63.4	98.5		0.356
	0.060	32.6	38.6	39.4	59.3	98.7		0.399
	0.100	35.0	42.5	44.3	58.8	103.1		0.430

Fig. 1—The Vanselow exchange constant, K_V, for montmorillonite and illite as a function of concentration at different equivalent fractions of exchangeable Ca E_{Ca}.

cation concentration, R'_{Na}, and on ion activities, R_{Na}. The ion activity coefficients in the solution were calculated from the extended form of the Debye-Hückel equation, which includes individual ion size parameters. Although the initial composition of the solutions, R'_{Na}, were 10, 20, and 40, and that of the exchange phase, E_{Na}, were 0.10, 0.20, and 0.40, respectively, the equilibrium R'_{Na} and E_{Na} values of the solutions were lower for both clays and the changes were more pronounced in the diluted solutions. A similar change in the solution composition also took place. For both clays, E_{Na} decreased with a decrease in the solution concentration. However, it should be noted that whereas in illite clay, the exchange phase is enriched with exchangeable Na during equilibrations, the reverse was true for montmorillonite. The illite data are easily understood. Calcium ions that have been released from the exchange phase induced the change in the R'_{Na} of the equilibrium solution. However, this explanation does not hold for the montmorillonite systems, where both the solution and exchange phases were enriched with Ca^{2+}. It seems that in montmorillonite systems, dissolution and hydrolysis of Ca-releasing primary minerals (Rhoades et al., 1968) is enough to enrich both phases with calcium ions. This conclusion is further supported by measured cation exchange capacity (CEC) of the clay as a function of adsorbed cation compositions. The CEC of Ca- and Na-illite was 17.71 and 14.56 meq/100 g, respectively, and for Ca- and Na-montmorillonite it was 105.7 and 79.5 meq/100 g, respectively. The CEC

of the two clays as a function of their composition is also presented in Table 2. It is evident that the CEC, as measured in this study, is a function of the exchangeable cation. It seems to us that in the process of preparing homoionic Na clay free of electrolytes, some of the adsorbed Na cations have hydrolyzed (Shainberg, 1973). However, the amount of exchangeable Ca was not affected by the desalting treatment mainly because the Ca ions from the Ca-releasing primary minerals (Rhoades et al., 1968) replace adsorbed Ca that was hydrolyzed. The release of Ca^{2+} from the primary minerals enhances the hydrolysis of exchangeable Na.

The effect of salt concentration of E_{Ca} on the affinity of the two clays for Ca^{2+}, expressed in terms of K_V, is given in Fig. 1. Whereas in illite clay the affinity of the clay for Ca^{2+} decreased with an increase in the fraction of exchangeable Ca, E_{Ca}, the reverse was true for montmorillonite clay. The decrease in affinity of the illite clay for Ca^{2+} with increasing E_{Ca} can be explained by two mechanisms. The first mechanism is derived from the diffuse double-layer theory and assumes uniform exchange sites. According to this explanation, the electrical potential in the diffuse double layer decreases as E_{Ca} increases, thus the preferential affinity of the clay for Ca^{2+} over Na^+ also decreases. The other explanation assumes that there are various exchange sites on the clay with various affinities for Ca^{2+}. With increasing E_{Ca}, the sites with the low affinity for Ca^{2+} are last to be occupied by the Ca ions. Thus the affinity for Ca^{2+} decreases with an increase in E_{Ca}. These two mechanisms should apply also to montmorillonite systems. However, in montmorillonite clay, the formation of quasicrystals and the presence of internal surfaces (Table 1) dominates and causes the affinity of the clay for Ca^{2+} to increase with increasing E_{Ca}.

The Vanselow selectivity coefficients for montmorillonite clay were almost unaffected by the total electrolyte concentration at concentrations above 30 meq/liter. These values were 3.7, 3.4, and 1.95 for E_{Ca} of 0.9, 0.8, and 0.6, respectively (Fig. 1). The values for $E_{Ca} = 0.6$ agreed with the values predicted by the diffuse double-layer equation (Table 1). At this E_{Ca} value, the quasicrystals are not stable (Shainberg and Otoh, 1968), and their effect on K_V is small, and the

Table 3—Experimental and predicted Gapon exchange constants.

Initial R'_{Na} and $E_{Na} \times 100$	Concentration	Gapon constants			
		Experimental (k'_G)		Theoretical (k_G)†	
		Montmorillonite	Illite	External surfaces	Internal surfaces
0.10	1	--	--	0.0315	0.0066
	3	0.0086	0.0199	-	-
	10	0.0095	0.0238	0.0287	0.0074
	30	0.0105	0.0255	-	-
	60	0.0106	0.0253	--	-
	100	0.0105	0.0250	0.0192	0.0100
0.20	1	--	--	0.0319	0.0110
	3	0.0103	0.0201	--	--
	10	0.0112	0.0215	0.0293	0.0114
	30	0.0118	0.0248	-	-
	60	0.0121	0.0227	-	-
	100	0.0127	0.0218	0.0224	0.0126
0.40	1	-	--	0.0340	0.0170
	3	0.0244	0.0263	-	-
	10	0.0217	0.0208	0.0330	0.0173
	30	0.0189	0.0211	-	--
	60	0.0202	0.0231	--	--
	100	0.0214	0.0219	0.0270	0.0172

† Because k_G is based on ion activities, it is about 15% greater than k'_G which is based on ion concentration.

agreement between predicted (assuming $Y_d = 0$) and experimental values for K_V is reasonable. Also, at this E_{Ca}, the K_V values for illite were similar to those of montmorillonite, suggesting again that in both clays at $E_{Ca} = 0.6$ (and values below $E_{Ca} = 0.6$), most of the clay surfaces were external. Similarly, at $E_{Ca} = 0.6$, dilution of the equilibrium solution resulted in reduced affinity for Ca^{2+} for both clays in agreement with the diffuse double-layer prediction for the external surfaces. All these observations support our previous conclusions that at this exchangeable ion composition the quasicrystals are not stable and most of the exchange reactions take place on the external surfaces.

The effect of concentration on K_V values of illite was not significant, with a trend to lower affinity for Ca^{2+} with dilution. This relation was similar to those predicted by Eq. [6] for external surfaces (Table 1) and suggests that internal surfaces do not play a dominant role on Na/Ca illite.

The effect of dilution on the K_V of montmorillonite at E_{Ca} of 0.8 and 0.9 was also not significant. However, in the low concentration end, the trend was for an increase in affinity for Ca^{2+} with dilution. van Bladel et al. (1972) reported a bigger effect. Their values for K'_c $(K'_c = E_{Ca} m_{Na}^2 / E_{Na}^2 m_{Ca})$ at an E_{Ca} of 0.8, were 5.0, 5.5, and 6.7 for 25, 10, and 5 meq/liter, respectively, and for $E_{Ca} = 0.9$, these values were 9.0, 9.0, and 14.8, respectively. Their findings supported the trend that we observed for $E_{Ca} \geqslant 0.8$, that the affinity of montmorillonite clay for Ca^{2+} increases with dilution, and that the effect of dilution is more pronounced the higher the E_{Ca}. The predicted exchange equation, which assumes the presence of internal surface, gives a similar trend.

The U. S. Salinity Laboratory Staff (1954) advocated the use of an empirical Gapon equation

$$E_{Na}/E_{Ca} = k_G' R_{Na}' \qquad [9]$$

where k_G' represents the Gapon selectivity coefficient calculated from total ion concentrations. Analysis of

a large number of soil samples led the U. S. Salinity Laboratory Staff (1954) to conclude that the value of k_G' is 0.01475, whereas Bower (1959) published a value of 0.0173. The experimental constants for illite and montmorillonite and the value predicted based on the diffuse double layer (without multipling the surface charge density by a factor of 1:2 and 1:4 (Bolt, 1955; and Bower, 1959, respectively) are presented in Table 3. When one compares the average k_G' value for soils with our experimental results, the following trends are evident:

a) The experimental Gapon selectivity coefficients for montmorillonite clay are lower than those reported by the U. S. Salinity Laboratory for soils with $E_{Na} \leqslant 0.2$. However, k_G' for montmorillonite clay with $E_{Na} > 0.2$ are larger than those for soils and are only slightly affected by the total salt concentration with a trend for the affinity for Na^+ to increase with increase in the salt concentration. Since the theoretical Gapon selectivity coefficients for internal surfaces follow similar trends, the Gapon selectivity coefficients for montmorillonite clay may be evaluated from the diffuse double-layer theory only when we recognize that most of the exchange takes place on internal surfaces.

b) The experimental Gapon selectivity coefficients for illite clay are higher than the average k_G' for soils and seem to be independent of the salt concentration.

c) The theoretical Gapon selectivity coefficients for external surfaces are higher than those observed for soils and for clays. In order to obtain a good agreement between the diffuse double-layer exchange equation and the experimental values, Bolt (1955) and Bower (1959) multiplied the surface charge density of the clays with a correction factor larger than 1.0. Increase in surface charge density of the clay leads to higher affinity of the clay for Ca^{2+} and lower k_G' values because of the increase in the negative electric potential at the clay surface.

Based on the above observations we may conclude that the Gapon selectivity coefficient is not expected to be constant. It is related to the Vanselow selectivity coefficient by the following equation:

$$k_G^2 = \frac{E_{Na} - 0.5 \, E_{Ca}}{2,000 \, K_V \, E_{Ca}} \qquad [10]$$

which indicates that k_G depends also on the composition of the exchange phase. It is also evident that k_G' value obtained for many soils is a weighted average of the mineralogy of the soils. It seems that for an "average" soil, which contains montmorillonite, illite, and kaolinite, a value for k_G' of 0.015 is obtained. However, "average" soil will deviate, depending on the mineralogy of the soil and the composition of the solution and exchange phases.

LITERATURE CITED

1. Babcock, K. L. 1963. Theory of the chemical properties of soil colloidal systems at equilibrium. Hilgardia 34:417–542.
2. Bar-On, P., and I. Shainberg. 1970. Hydrolysis and decomposition of Na-montmorillonite leached with distilled water. Soil Sci. 109:241–246.
3. Bolt, G. H. 1955. Ion absorption of clays. Soil Sci. 79:267–

276.

4. Bower, C. A. 1959. Cation exchange equilibria in soils affected by sodium salts. Soil Sci. 88:32–35.

5. Eriksson, E. 1952. Cation exchange equilibria on clay minerals. Soil Sci. 74:103–118.

6. Levy, R., and D. Hillel. 1968. Thermodynamic equilibrium constants of sodium-calcium exchange in some Israel soils. Soil Sci. 106:393–398.

7. Rhoades, J. D., D. B. Krueger, and M. J. Reed. 1968. The effect of soil mineral weathering on the sodium hazard of irrigation water. Soil Sci. Soc. Am. Proc. 32:643–647.

8. Shainberg, I. 1973. Rate and mechanisms of Na-montmorillonite hydrolysis in suspensions. Soil Sci. Soc. Am. Proc. 37: 689–694.

9. Shainberg, I., and H. Otoh. 1968. Size and shape of montmorillonite particles saturated with Na/Ca ions. Israel J. Chem. 6:251–259.

10. Sposito, G. 1977. The Gapon and the Vanselow selectivity coefficients. Soil Sci. Soc. Am. J. 41:1205–1206.

11. Sposito, G., and S. V. Mattigod. 1979. Ideal behavior in Na^+ — trace metal cation exchange on Camp Berteau montmorillonite. Clays Clay Miner. 27:125–128.

12. U. S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. USDA Agric. Handb. no. 60.

13. van Bladel, R., G. Gavira, and H. Laudelout. 1972. A comparison of the thermodynamic, double-layer theory and empirical studies of the Na-Ca exchange equilibria in clay water systems. Proc. Int. Clay Conf., p. 385–398.

14. van Olphen, H. 1977. An introduction to clay colloid chemistry, 2nd ed. John Wiley & Sons, New York.